

MONTE-CARLO SIMULATION OF- DISC LIKE MOLECULES WITH GAY-BERNE TYPE PAIR INTERACTION POTENTIAL

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Abstract : This work reports a Monte-Carlo simulation in a system of discotic liquid crystal molecules interacting via Gay-Berne pair interaction potential. This simulation is able to generate columnar phase.

Keywords : single site potential, thermotropic liquid crystal, columnar phase.

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1. Introduction

Dispersive forces between molecules are believed to be primarily responsible for giving rise to liquid crystalline phases. But the anisotropy of the short range intermolecular repulsions also play important role in determining the phases. To take care of both attractive and repulsive forces in a phenomenological manner, at the earlier stage of computer simulations of aspherical molecules, several sites on each molecule were chosen between which Lennard-Jones potential could act. Later works avoided the computational

inefficiency of this type of site-site potential for large molecules by replacing it with a single site potential. In an attempt to provide computationally simple realistic potential Gay and Berne [1] proposed a potential based on the Gaussian overlap model potential [2]. They modelled a single site potential for rod like molecules by fitting it with the site-site potential for a linear array of atoms. The potential is of the form

$$U(\hat{u}_1, \hat{u}_2, \hat{r}) = 4 (\hat{u}_1, \hat{u}_2, \hat{r}) \times \left[\left(\frac{\sigma_0}{r - \sigma(\hat{u}_1, \hat{u}_2, \hat{r}) + \sigma_0} \right)^6 - \left(\frac{\sigma_0}{r - \sigma(\hat{u}_1, \hat{u}_2, \hat{r}) + \sigma_0} \right)^{12} \right]$$

where \hat{u}_1, \hat{u}_2 are unit vectors giving the orientations of the two particles, \hat{r} is the intermolecular vector and r is the molecular separation. $\epsilon(\hat{u}_1, \hat{u}_2, \hat{r})$ is the well depth and $\sigma(\hat{u}_1, \hat{u}_2, r)$ is the distance of nearest approach which can be expressed as

$$\sigma(\hat{u}_1, \hat{u}_2, \hat{r}) = \sigma_0 \left[1 - \chi \left\{ \frac{(\hat{r} \cdot \hat{u}_1 + \hat{r} \cdot \hat{u}_2)}{1 + \chi(\hat{u}_1 \cdot \hat{u}_2)} + \frac{(\hat{r} \cdot \hat{u}_1 - \hat{r} \cdot \hat{u}_2)}{1 - \chi(\hat{u}_1 \cdot \hat{u}_2)} \right\} \right]^{-1/2}$$

where the shape anisotropy parameter

$$\chi = [(\sigma_{\parallel} / \sigma_{\perp})^2 - 1] / [(\sigma_{\parallel} / \sigma_{\perp})^2 - 1]$$

\parallel and \perp mean parallel and perpendicular to the intermolecular vector respectively.

The well depth

$$\epsilon(\hat{u}_1, \hat{u}_2, \hat{r}) = \epsilon_0 \epsilon^V(\hat{u}_1, \hat{u}_2) \epsilon^M(\hat{u}_1, \hat{u}_2, \hat{r})$$

$$\text{where} \quad \epsilon(\hat{u}_1, \hat{u}_2) = [1 - \chi^2 (\hat{u}_1 \cdot \hat{u}_2)^2]^{-1/2}$$

$$\epsilon'(u_1, u_2, r) = 1 - \frac{1}{2} \chi' \left[\frac{(\hat{r} \cdot \hat{u}_1 + \hat{r} \cdot \hat{u}_2)}{1 + \chi' (u_1 \cdot u_2)} + \frac{(\hat{r} \cdot \hat{u}_1 - \hat{r} \cdot \hat{u}_2)^2}{1 - \chi' (\hat{u}_1 \cdot \hat{u}_2)} \right]$$

with the well depth anisotropy parameter

$$\chi' = [1 - (\epsilon_{||} / \epsilon_{\perp})^{1/\mu}] / [1 + (\epsilon_{||} / \epsilon_{\perp})^{1/\mu}]$$

where $\epsilon_{||}$ and ϵ_{\perp} refer to well depth with parallel and perpendicular relative orientations of the two molecules respectively and μ and χ are adjustable parameters.

In the following we report the simulation of columnar phase for disc-like molecules interacting via Gay-Berne type pair interaction potential using Monte-Carlo simulation technique. The parameters of the potential are so chosen that it can approximate the behaviour of disc-like molecules. For disc-like molecules

$$\chi = [(\sigma_e / \sigma_s)^2 - 1] / [(\sigma_e / \sigma_s)^2 + 1]$$

σ_e is the separation between two interacting molecules when they are in end-end configuration just touching each other; σ_s is the separation for side-side configuration. So, σ_s and σ_e are equal to the diameter and width respectively. The value of χ is negative for disc-like molecules. Similarly,

$$\chi' = [1 - (\epsilon_e / \epsilon_s)] / [1 + (\epsilon_e / \epsilon_s)]$$

where ϵ_s and ϵ_e are well depths at side-side and end-end configuration. For the side-side configuration of disc-like molecules $\hat{u}_1 \parallel \hat{u}_2$, $\hat{u}_1, \hat{u}_2 \perp \hat{r}$. This gives $\sigma(\hat{u}_1, \hat{u}_2, \hat{r}) = \sigma_0$. So we take $\sigma_0 = \sigma_s$ for our calculation.

2. Monte-Carlo simulation

For Monte-Carlo simulation we have chosen a $10 \times 10 \times 10$ lattice system. In the initial configuration all the molecular short axes are parallel to laboratory Z-axis and the centres of mass of molecules are placed on regular square lattice points in each plane parallel to laboratory X-Y plane. The intermolecular distance between a molecule and its nearest neighbour along X or Y axis are set equal to 1 but along Z it is equal to $a = \sigma_s / \sigma_e$. This value of 'a' assures uniform density along the three directions when a columnar phase is stabilised. Metropolis algorithm is used to equilibrate the system. But the translational motion of the molecules are controlled in such a way that it cannot go out of the cell it belongs i.e. the neighbours of the molecules are kept fixed. This restriction is more or less valid in a very dense system like discotic liquid crystal which has isotropy in one direction only in columnar phase. All the molecules are treated in the same manner and we get the final configuration of the lattice as a whole. The total procedure constitutes an iteration. Iterations are performed till equilibrium is reached. At the production stage of simulation we first get random position co-ordinates (Fig1) by finding an equilibrium isotropic distribution at a very large $T=100$. Then we lowered the temperature considerably to $T=0.1$. The distribution of molecular centers of mass on XZ

plane (Fig2) shows that columns are formed along Z direction. Centre of mass positions on XY plane shows rectangular lattice structure (Fig3). The values of parameters ν and μ are taken equal to 2 and 1 respectively. We take

$\sigma_c/\sigma_s=1/3$ and $\epsilon/\epsilon_c=1/5$; diameter of a molecule $r=0.9$. The simulation was performed at constant volume condition. After

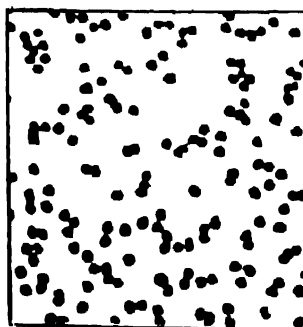


Fig 1. Random distribution of the centre of mass of molecules at $T=100$.

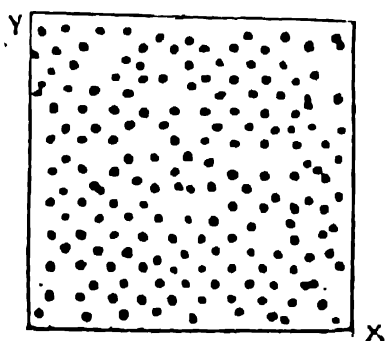


Fig 2. Square arrangement of molecules on X-Y plane (Z is parallel to the director) at $T=0.1$

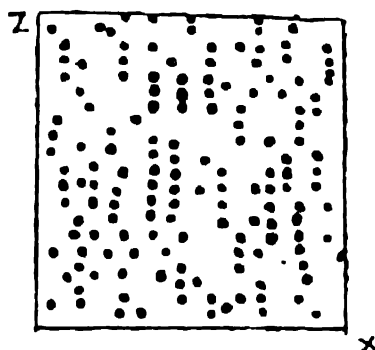


Fig 3. Arrangement of molecules on X-Z plane shows column formation along Z axis.

each iteration the orientational order parameter $\eta=\langle P_2(\cos\theta) \rangle$ are calculated. The criterion for equilibrium is that the difference in average value of order parameters for successive 1000 configurations is stable within 5%.

3. Conclusion

This computer simulation shows that the Gay-Berne interaction stabilizes to a columnar phase with square arrangement of molecular centers of mass in planes perpendicular to the columnar phase. This type of columnar phase is seen in lyotropic system and not in thermotropic disc-like mesogens where the columnar phases are rectangular or hexagonal. The same conclusion was reached by Emerson et al [3] from their molecular dynamics study of disc like Gay Berne mesogens. The present work supports their findings. The structure obtained in the present work as well as in the molecular dynamics study is believed to be due to strong correlation between discs in neighbouring columns with molecules fitting into the grooves of a neighbour. These grooves are the result of the elliptical cross-section of molecules and interdigitation is a hindrance towards forming a hexagonal phase. Further studies are indeed called for reproducing a rectangular or a hexagonal phase.

References

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